

PATENT ABSTRACTS OF JAPAN

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(54) SOLID POLYMER ELECTROLYTE MEMBRANE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid polymer electrolyte membrane suitable for a fuel cell excellent in mechanical strength and heat resistance.

SOLUTION: This solid polymer electrolyte membrane comprises a composite of a porous thin film having 300 g or more of film-penetrating strength and 300° C of mechanical heat-resistance temperature in the film and a proton-conductive polymer electrolyte. A content of the proton-conductive polymer electrolyte in the solid polymer electrolyte membrane is 30-85 wt.%, and the porous thin film is a high strength high-gas-permeable porous thin film supporting body having 50 μm or less of average film thickness, 200 g or more of penetrating strength, and 10 sec/100 cc.in² or less of gas-permeability.

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CLAIMS

[Claim(s)]

[Claim 1] The membranous solid-state mold polymer electrolyte membrane of proton conductivity whose reinforcement is 300g or more and whose membranous dynamic heat-resistant temperature it thrusts and is 300 degrees C or more.

[Claim 2] The solid-state mold polymer electrolyte membrane of claim 1 which is the complex of a porosity thin film and the polymer electrolyte of proton conductivity.

[Claim 3] The solid-state mold polymer electrolyte membrane according to claim 1 to 2 characterized by the content of the proton conductivity polymer electrolyte in this solid-state mold polymer electrolyte membrane being 30 - 85 % of the weight.

[Claim 4] The solid-state mold polymer electrolyte membrane according to claim 2 to 3 characterized by for average thickness thrusting [this porosity thin film] by 50 micrometers or less, and for reinforcement being 200g or more, and air permeability being the porosity thin film base material of two or less cc-in [10sec(s)/100 cc-in] high intensity and high air permeability.

[Claim 5] The solid-state mold polymer electrolyte membrane according to claim 4 characterized by being the film which much pores which consist of sheet or aramid resin of Mr. Kami who has the permeability of the structure which the synthetic pulp which is the polymer of all aromatic polyamide distributes in the clearance between the nonwoven fabric with which the porosity thin film base material of this high intensity and high air permeability consists of an aramid fiber which are all aromatic polyamide polymers, textiles, or an aramid fiber opened.

[Claim 6] The solid-state mold polymer electrolyte membrane according to claim 5 characterized by being the sheet of the shape of the amounts 12-30g of superintendent officers which the porosity thin film base material of this high intensity and high air permeability becomes from all aromatic polyamide polymers/a nonwoven fabric of m2.

[Claim 7] The solid-state polymer electrolyte membrane of claims 2-6 this whose complex is impregnation unification complex of a porosity thin film and a polymer electrolyte.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the solid-state mold polymer electrolyte membrane suitable for the fuel cell excellent in mechanical strength and thermal resistance.

[0002]

[Description of the Prior Art] ***** to which a new energy technique is brought into the limelight with the close-up of an environmental problem in recent years. The fuel cell technique is positioned as one of the columns of these new energy technique. The polymer electrolyte fuel cell (PEFC) using the polyelectrolyte film of proton conductivity attracts attention as an electrolyte especially as a power source for loading to which small lightweight-ization makes an electric vehicle the start from the description of possible **.

[0003] As polyelectrolyte film for polymer electrolyte fuel cells, Nafion R (Du Pont trademarks, such as Nafion 115 and 117) which is the perphloro polymer of super-strong acid radical content, for example is known. This is widely used as an ingredient with which not only ion exchange capacity is comparatively high, but the mechanical strength is comparatively excellent with 0.91 milliequivalent / g resin. It is known that membrane resistance will fall and a big current can be taken out, so that it depends on resistance of an electrolyte membrane for the current density which can be taken out in the fuel cell using this, the film is thin-film-ized and the degree of swelling of water is raised. However, when this electrolyte membrane was used, thickness was made thin from the aforementioned viewpoint, for example an electrolyte membrane and an electrode were joined by hot pressing, the film was damaged, leak of gas was produced and there was a problem which an inter-electrode short circuit produces. Moreover, the approach of putting an electrolyte membrane mechanically, without using a hotpress in order to avoid this problem, and assembling a cel is also proposed. However, even when this technique is adopted, in order to keep junction to an electrode constant, it was required to put a remarkable pressure and it had the same trouble as hot pressing. Moreover, since the mechanical strength in the water swelling condition of an electrolyte membrane was not enough even when a cel is assembled somehow or other, there was a problem of concurring with a short circuit or a gas leak in a long-term activity.

[0004] As mentioned above, as an approach of improving the mechanical characteristic (at the time of cel production and a water swelling condition) of the electrolyte membrane represented by Nafion R, the impregnation unification of this polyelectrolyte is carried out at the drawing tetra-FURORO ethylene porous membrane opening section, and the compound-die electrolyte membrane which reinforced the mechanical characteristic of an electrolyte membrane is indicated by JP,8-162132,A. However, in the case of this technique, the porous membrane adopted as a base material is not only expensive, but since that surface tension was small, it had the trouble that a dope could not sink in easily, from the wettability problem of the dope at the time of sinking in a actual electrolyte dope.

[0005]

[Problem(s) to be Solved by the Invention] as mentioned above, the mechanical characteristic was excellent from a viewpoint of utilization of a polymer electrolyte fuel cell -- a thin film -- although development of the polymer electrolyte membrane [-izing / an electrolyte membrane] of proton conductivity is considered, the polymer electrolyte membrane which was still excellent practical is in the situation which is not found out.

[0006] As a result of inquiring wholeheartedly in view of such a situation, it came to complete a header and this invention for the approach of developing the solid-state mold polymer electrolyte membrane excellent in the practical use side which combines practical high proton conductivity, the strong short circuit

prevention reinforcement as a separator, and the high thermal resistance about short circuit prevention. The object of this invention is to offer the solid-state mold polymer electrolyte membrane for fuel cells which combines proton conductivity and reinforcement with three heat-resistant persons.

[0007]

[Means for Solving the Problem] This invention is pierced, it is the solid-state mold polymer electrolyte of proton conductivity whose reinforcement is 300g or more and whose membranous dynamic heatproof temperature is 300 degrees C or more, and it consists of complex of a porosity thin film and a proton conductivity polymer electrolyte. As for the content of the polymer electrolyte in this solid-state mold polymer electrolyte membrane, it is desirable that it is 30 - 85 % of the weight. Average thickness thrusts [this porosity thin film] by 50 micrometers or less. Reinforcement moreover, by 200g or more And the porosity thin film base material of that air permeability is the porosity thin film base material of two or less cc-in [10sec(s)/100 cc-in] high intensity and high air permeability, and its high intensity and high air permeability The nonwoven fabric, textiles which consist of an aramid fiber which are all aromatic polyamide polymers, Or it is the film which much pores which consist of sheet or aramid resin of Mr. Kami who has the permeability of the structure which the synthetic pulp which is the polymer of all aromatic polyamide distributes in the clearance between aramid fibers opened, Or as for the porosity thin film base material of this high intensity and high air permeability, it is desirable that it is the sheet of the shape of the amounts 12-30g of superintendent officers which consist of all aromatic polyamide polymers/a nonwoven fabric of m2, and, as for this complex, it is still more desirable that it is really [of a porosity thin film and a polymer electrolyte / impregnation] complex.

[0008]

[Embodiment of the Invention] Hereafter, the solid-state mold polymer electrolyte of this invention is explained further. The solid-state mold polymer electrolyte membrane of this invention is a polymer electrolyte membrane which combines the practical proton conductivity of sufficient 300g or more to apply to a fuel cell which thrusts, and shows reinforcement and has the dynamic heat-resistant temperature of 300 degrees C or more, and the outstanding heat mechanical characteristic.

[0009] In the case of the solid-state mold polymer electrolyte membrane of this invention, it thrusts and it is the description that reinforcement is also as high as 300g or more. It thrust, and it is the physical properties used for assessment of a separator as an index showing the short circuit prevention reinforcement of the separator of the present solution mold lithium ion secondary site, and in this invention, reinforcement pierced the value measured on condition that the following, and made it reinforcement.

[0010] The solid-state mold polymer electrolyte membrane was set to the fixed frame of 11.3mmphi, the needle with a point radius of 0.5mm was pierced at right angles to the center of a base material, the needle was pushed in with 50mm constant speed for /, the force concerning a needle when a hole opens to a base material was pierced, and it considered as reinforcement.

[0011] When this value is less than 300g, this polymer electrolyte membrane thrusts, and reinforcement becomes less enough and it becomes less desirable [increase / the short circuit probability of occurrence of the electrodes in the hotpress process at the time of finishing setting up a cell or a membranous gas leak probability / and].

[0012] Moreover, the dynamic point 300 degrees C or more of the polymer electrolyte membrane of this invention of ***** (ing) is the description. Here, dynamic heat-resistant temperature was measured on condition that the following.

[0013] A 1g load is applied to the polymer electrolyte membrane of the shape of a strip of paper with the thickness of about 45 micrometers, a width of face [of 5mm], and a die length of 25mm, namely, temperature up of the temperature was carried out the rate for 10-degree-C/by the load of 0.0044g [micrometer] /and mm, heat mechanical property analysis (TMA) was carried out and temperature to which the film fractures or the film is extended 10% was made into dynamic heat-resistant temperature.

[0014] It becomes impossible for this temperature to guarantee the stability of the cell at the time of the internal temperature of a cell going up rapidly by an anomalous reaction etc. at less than 300 degrees C, and it is not desirable. The solid-state mold polymer electrolyte membrane of this invention is produced by compound-izing the porosity base material thin film which has the description in reinforcement and thermal resistance, and the polymer electrolyte which has sufficient proton conductivity practical. The content of the polymer electrolyte in that case has 30 - 85% of the weight of the desirable range. When a polymer electrolyte content compound-izes with a porosity base material at less than 30 % of the weight, sufficient proton conductivity is not acquired and it is not desirable. When the content increases more than 85 % of the weight, it becomes moreover, less desirable [increase / the reinforcement of bipolar membrane falls

or / the thickness of a polymer electrolyte membrane / and].

[0015] Next, the polymer electrolyte of proton conductivity which the porosity base material of this invention is made to form into impregnation compound is explained. The proton conductivity polymer electrolyte which has the high ion exchange group equivalent it was presupposed that it is not limited and there was a problem conventionally in mechanical characteristic especially as a polymer electrolyte used for this invention is also possible by concomitant use of a porosity base material. The sulfonic-acid polymer which has a perphloro frame which is represented by Nafion R as a concrete polymer electrolyte, sulfonation polysulfone, sulfonation polyether sulphone, a sulfonation polyether ether ketone, etc. are mentioned. However, the polymer of the type which can carry out direct impregnation coating to a porosity thin film base material from the polymer of a floating (solution) condition is more suitably used from the ease of a film production process.

[0016] Next, the porosity base material thin film used for this invention is explained. As a porosity base material thin film of this invention, average thickness is 50 micrometers or less, it thrusts, and reinforcement is 200g or more, and two or less cc-in [10sec(s)/100 cc-in] high intensity and a high air permeability thin film are suitably used for air permeability. Since the thickness of the polymer electrolyte bipolar membrane obtained will become thick although it becomes easy to obtain the base material of high intensity if average thickness is set to 50 micrometers or more, the degree of swelling to the water of an electrolyte membrane falls, and membrane resistance becomes less desirable [go up and].

[0017] The base material of this invention thrusts and a thing 200g or more is suitably used as reinforcement. When this value uses a base material lower than 200g, also after carrying out impregnation of the polymer electrolyte and compound-izing it, the thing 300g or more for which it thrusts and reinforcement is realized becomes difficult, and this better ** does not exist.

[0018] The air permeability of the base material of this invention shows the value measured by the gar rhe method (time amount from which 100 cc air requires 1 inch of area of 2 for penetrating by the pressure of 2.3cmHg(s)). As a porosity base material thin film of this invention, the base material which this value shows two or less cc-in [10sec/100 cc-in] high air permeability is used suitably. When this value uses the low base material of larger air permeability than 10sec / 100 cc-in², while impregnation compound-ization of the polymer electrolyte by the coating method from the polymer solution considered to be industrial the most advantageous becomes difficult, the proton conductivity of a compound polymer electrolyte becomes [fully raising] difficult and is not desirable, either.

[0019] As an ingredient for the porosity thin film base materials of the high intensity and high air permeability of this invention, the polyamide of all aromatic series is preferably used from reinforcement and a heat-resistant viewpoint. A film with the permeability which many holes which consist of aramid resin which is the nonwoven fabric which consists of an aramid fiber which is the polymer of all aromatic polyamide as the base material configuration, textiles, the sheet of Mr. Kami who has the permeability which the synthetic pulp which is the polymer of all aromatic polyamide distributes in the clearance between the aramid fiber, or the polymer of all aromatic polyamide opened etc. can be mentioned. If the need property as the above mentioned base material is satisfied, it is possible to use the thing of every configuration for this invention among these, but when air permeability is taken into consideration, a nonwoven fabric-like sheet is used most suitably. As the amount of superintendent officers, the range of 12 - 30 g/m² is used suitably. Although it becomes easy to obtain the high base material of air permeability when the amount of superintendent officers is less than [12g //m] two, it becomes difficult to thrust and to obtain a thing 200g or more as reinforcement, and it becomes impossible to obtain the solid-state mold electrolyte membrane which was excellent in the mechanical characteristic as a result. On the other hand, although it will become easy to thrust and to satisfy reinforcement if the amount of superintendent officers increases more than 30 g/m², it becomes difficult to obtain the base material of 50 micrometers or less of average thickness. Moreover, if a consistency is formed into a raising thin film by force, it becomes difficult and is not desirable for air permeability to fall and to obtain the high bipolar membrane of proton conductivity as a result.

[0020] As the molecular structure of all aromatic polyamide polymers, it is available to this invention regardless of a metasystem and the Para system. With a metasystem, all the aromatic polyamide that makes m-phenylene isophthalamide a main configuration unit is mentioned as a typical thing, and it is mentioned here as what has all the aromatic polyamide typical [the Para system] that makes p-phenylene terephthalamide a main configuration unit.

[0021] Moreover, the porosity base material of this invention may cover the front face with a metallic oxide etc. if needed, and may raise the oxidation resistance of a base material. The coat by the metallic oxide can be performed by immersing said porous base material thin film in the gel product solutions (alcohol

etc.) of the shape of a solution which made hydrolysis nature organic metal compounds, such as a metal alkoxide, react with water, and made them specifically gel selectively, being immersed subsequently to water, and drying at the temperature around [after promoting a reaction] 200 degrees C.

[0022]

[Example] Hereafter, the content of this invention is explained to a detail using an example.

[0023] [Example 1]

The amorphous-sized m-aramid continuous glass fiber of size 3de was added as a binder to m-aramid staple fiber which <aramid base material> size 1.25de crystallized, the film was produced by amount of superintendent officers 19 g/m² by the dry type milling-paper method, the calendering roll was covered, and the nonwoven fabric-like sheet was obtained. The property of the obtained base material was as follows. 36 micrometers of average thickness, consistency 0.53 g/cm³, 62% of voidage, and air permeability 0.04sec/100 cc-in² -- thrusting -- the reinforcement of 330g.

[0024] Using perphloro sulfonic-acid (Nafion) resin as polymer resin for the electrolytes of <compound-sized of polymer electrolyte> proton conductivity, 5% solution (Nafion; Aldrich make) of this was dried at 80 degrees C after impregnation and coating to the aforementioned aramid base material for 2 hours, and the Nafion bipolar membrane was produced. The property of the obtained bipolar membrane was as follows. 40 micrometers of thickness, and the 60 % of the weight of the amounts of Nafion impregnation, it thrusts and they are the reinforcement of 450g, and the TMA heatproof temperature of 400 degrees C or more.

[0025] Using the electrode made from U.S. E-TEKINC which made the platinum of 0.38 mg/cm² support as a <fuel cell cel production> gas diffusion electrode, this was pierced to 30mmphi and it considered as the gas diffusion electrode. After being immersed for 2 hours into the ion exchange water which boiled the aforementioned compound electrolyte membrane and making the film into a moisture state, surface superfluous water was wiped off, and it put with two gas diffusion electrodes, and pressurized for 3 minutes by 100 Kgf/cm² at 100 degrees C, and the electrode zygote was obtained. About the obtained electrode complex, humidification hydrogen and oxygen were supplied and fuel cell output characteristics were evaluated under 80-degree-C heating. Although ten single cels were produced, defects, such as a short circuit and a gas leak, do not have one, and the engine performance of 0.65V was obtained by 0.7 A/cm².

[0026] The electrolyte membrane of Nafion independent 40-micrometer thickness was produced without using an aramid base material in the [example 1 of comparison] example 1. The fuel cell single cel was produced like the example 1 using the obtained film. The defect (a short circuit, gas leak) was accepted in three of ten produced single cels, and production of the stable thin film cel was difficult.

[0027]

[Effect of the Invention] According to this invention, it becomes possible to provide with a useful solid-state mold polymer electrolyte membrane the polymer electrolyte fuel cell application which has the outstanding proton conductivity and the outstanding heat mechanical characteristic.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the solid-state mold polymer electrolyte membrane suitable for the fuel cell excellent in mechanical strength and thermal resistance.

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PRIOR ART

[Description of the Prior Art] ***** to which a new energy technique is brought into the limelight with the close-up of an environmental problem in recent years. The fuel cell technique is positioned as one of the columns of these new energy technique. The polymer electrolyte fuel cell (PEFC) using the polyelectrolyte film of proton conductivity attracts attention as an electrolyte especially as a power source for loading to which small lightweight-ization makes an electric vehicle the start from the description of possible **.

[0003] As polyelectrolyte film for polymer electrolyte fuel cells, Nafion R (Du Pont trademarks, such as Nafion 115 and 117) which is the perphloro polymer of super-strong acid radical content, for example is known. This is widely used as an ingredient with which not only ion exchange capacity is comparatively high, but the mechanical strength is comparatively excellent with 0.91 milliequivalent / g resin. It is known that membrane resistance will fall and a big current can be taken out, so that it depends on resistance of an electrolyte membrane for the current density which can be taken out in the fuel cell using this, the film is thin-film-ized and the degree of swelling of water is raised. However, when this electrolyte membrane was used, thickness was made thin from the aforementioned viewpoint, for example an electrolyte membrane and an electrode were joined by hot pressing, the film was damaged, leak of gas was produced and there was a problem which an inter-electrode short circuit produces. Moreover, the approach of putting an electrolyte membrane mechanically, without using a hotpress in order to avoid this problem, and assembling a cel is also proposed. However, even when this technique is adopted, in order to keep junction to an electrode constant, it was required to put a remarkable pressure and it had the same trouble as hot pressing. Moreover, since the mechanical strength in the water swelling condition of an electrolyte membrane was not enough even when a cel is assembled somehow or other, there was a problem of concurring with a short circuit or a gas leak in a long-term activity.

[0004] As mentioned above, as an approach of improving the mechanical characteristic (at the time of cel production and a water swelling condition) of the electrolyte membrane represented by Nafion R, the impregnation unification of this polyelectrolyte is carried out at the drawing tetra-FURORO ethylene porous membrane opening section, and the compound-die electrolyte membrane which reinforced the mechanical characteristic of an electrolyte membrane is indicated by JP,8-162132,A. However, in the case of this technique, the porous membrane adopted as a base material is not only expensive, but since that surface tension was small, it had the trouble that a dope could not sink in easily, from the wettability problem of the dope at the time of sinking in a actual electrolyte dope.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, it becomes possible to provide with a useful solid-state mold polymer electrolyte membrane the polymer electrolyte fuel cell application which has the outstanding proton conductivity and the outstanding heat mechanical characteristic.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] as mentioned above, the mechanical characteristic was excellent from a viewpoint of utilization of a polymer electrolyte fuel cell -- a thin film -- although development of the polymer electrolyte membrane [-izing / an electrolyte membrane] of proton conductivity is considered, the polymer electrolyte membrane which was still excellent practical is in the situation which is not found out.

[0006] As a result of inquiring wholeheartedly in view of such a situation, it came to complete a header and this invention for the approach of developing the solid-state mold polymer electrolyte membrane excellent in the practical use side which combines practical high proton conductivity, the strong short circuit prevention reinforcement as a separator, and the high thermal resistance about short circuit prevention. The object of this invention is to offer the solid-state mold polymer electrolyte membrane for fuel cells which combines proton conductivity and reinforcement with three heat-resistant persons.

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MEANS

[Means for Solving the Problem] This invention is pierced, it is the solid-state mold polymer electrolyte of proton conductivity whose reinforcement is 300g or more and whose membranous dynamic heatproof temperature is 300 degrees C or more, and it consists of complex of a porosity thin film and a proton conductivity polymer electrolyte. As for the content of the polymer electrolyte in this solid-state mold polymer electrolyte membrane, it is desirable that it is 30 - 85 % of the weight. Average thickness thrusts [this porosity thin film] by 50 micrometers or less. Reinforcement moreover, by 200g or more And the porosity thin film base material of that air permeability is the porosity thin film base material of two or less cc-in [10sec(s)/100 cc-in] high intensity and high air permeability, and its high intensity and high air permeability The nonwoven fabric, textiles which consist of an aramid fiber which are all aromatic polyamide polymers, Or it is the film which much pores which consist of sheet or aramid resin of Mr. Kami who has the permeability of the structure which the synthetic pulp which is the polymer of all aromatic polyamide distributes in the clearance between aramid fibers opened, Or as for the porosity thin film base material of this high intensity and high air permeability, it is desirable that it is the sheet of the shape of the amounts 12-30g of superintendent officers which consist of all aromatic polyamide polymers/a nonwoven fabric of m2, and, as for this complex, it is still more desirable that it is really [of a porosity thin film and a polymer electrolyte / impregnation] complex.

[0008]

[Embodiment of the Invention] Hereafter, the solid-state mold polymer electrolyte of this invention is explained further. The solid-state mold polymer electrolyte membrane of this invention is a polymer electrolyte membrane which combines the practical proton conductivity of sufficient 300g or more to apply to a fuel cell which thrusts, and shows reinforcement and has the dynamic heat-resistant temperature of 300 degrees C or more, and the outstanding heat mechanical characteristic.

[0009] In the case of the solid-state mold polymer electrolyte membrane of this invention, it thrusts and it is the description that reinforcement is also as high as 300g or more. It thrust, and it is the physical properties used for assessment of a separator as an index showing the short circuit prevention reinforcement of the separator of the present solution mold lithium ion secondary site, and in this invention, reinforcement pierced the value measured on condition that the following, and made it reinforcement.

[0010] The solid-state mold polymer electrolyte membrane was set to the fixed frame of 11.3mmphi, the needle with a point radius of 0.5mm was pierced at right angles to the center of a base material, the needle was pushed in with 50mm constant speed for /, the force concerning a needle when a hole opens to a base material was pierced, and it considered as reinforcement.

[0011] When this value is less than 300g, this polymer electrolyte membrane thrusts, and reinforcement becomes less enough and it becomes less desirable [increase / the short circuit probability of occurrence of the electrodes in the hotpress process at the time of finishing setting up a cell or a membranous gas leak probability / and].

[0012] Moreover, the dynamic point 300 degrees C or more of the polymer electrolyte membrane of this invention of ***** (ing) is the description. Here, dynamic heat-resistant temperature was measured on condition that the following.

[0013] A 1g load is applied to the polymer electrolyte membrane of the shape of a strip of paper with the thickness of about 45 micrometers, a width of face [of 5mm], and a die length of 25mm, namely, temperature up of the temperature was carried out the rate for 10-degree-C/by the load of 0.0044g [micrometer] /and mm, heat mechanical property analysis (TMA) was carried out and temperature to which the film fractures or the film is extended 10% was made into dynamic heat-resistant temperature.

[0014] It becomes impossible for this temperature to guarantee the stability of the cell at the time of the internal temperature of a cell going up rapidly by an anomalous reaction etc. at less than 300 degrees C, and it is not desirable. The solid-state mold polymer electrolyte membrane of this invention is produced by compound-izing the porosity base material thin film which has the description in reinforcement and thermal resistance, and the polymer electrolyte which has sufficient proton conductivity practical. The content of the polymer electrolyte in that case has 30 - 85% of the weight of the desirable range. When a polymer electrolyte content compound-izes with a porosity base material at less than 30 % of the weight, sufficient proton conductivity is not acquired and it is not desirable. When the content increases more than 85 % of the weight, it becomes moreover, less desirable [increase / the reinforcement of bipolar membrane falls or / the thickness of a polymer electrolyte membrane / and].

[0015] Next, the polymer electrolyte of proton conductivity which the porosity base material of this invention is made to form into impregnation compound is explained. The proton conductivity polymer electrolyte which has the high ion exchange group equivalent it was presupposed that it is not limited and there was a problem conventionally in mechanical characteristic especially as a polymer electrolyte used for this invention is also possible by concomitant use of a porosity base material. The sulfonic-acid polymer which has a perphloro frame which is represented by Nafion R as a concrete polymer electrolyte, sulfonation polysulfone, sulfonation polyether sulphone, a sulfonation polyether ether ketone, etc. are mentioned. However, the polymer of the type which can carry out direct impregnation coating to a porosity thin film base material from the polymer of a floating (solution) condition is more suitably used from the ease of a film production process.

[0016] Next, the porosity base material thin film used for this invention is explained. As a porosity base material thin film of this invention, average thickness is 50 micrometers or less, it thrusts, and reinforcement is 200g or more, and two or less cc-in [10sec(s)/100 cc-in] high intensity and a high air permeability thin film are suitably used for air permeability. Since the thickness of the polymer electrolyte bipolar membrane obtained will become thick although it becomes easy to obtain the base material of high intensity if average thickness is set to 50 micrometers or more, the degree of swelling to the water of an electrolyte membrane falls, and membrane resistance becomes less desirable [go up and].

[0017] The base material of this invention thrusts and a thing 200g or more is suitably used as reinforcement. When this value uses a base material lower than 200g, also after carrying out impregnation of the polymer electrolyte and compound-izing it, the thing 300g or more for which it thrusts and reinforcement is realized becomes difficult, and this better ** does not exist.

[0018] The air permeability of the base material of this invention shows the value measured by the gar rhe method (time amount from which 100 cc air requires 1 inch of area of 2 for penetrating by the pressure of 2.3cmHg(s)). As a porosity base material thin film of this invention, the base material which this value shows two or less cc-in [10sec/100 cc-in] high air permeability is used suitably. When this value uses the low base material of larger air permeability than 10sec / 100 cc-in², while impregnation compound-ization of the polymer electrolyte by the coating method from the polymer solution considered to be industrial the most advantageous becomes difficult, the proton conductivity of a compound polymer electrolyte becomes [fully raising] difficult and is not desirable, either.

[0019] As an ingredient for the porosity thin film base materials of the high intensity and high air permeability of this invention, the polyamide of all aromatic series is preferably used from reinforcement and a heat-resistant viewpoint. A film with the permeability which many holes which consist of aramid resin which is the nonwoven fabric which consists of an aramid fiber which is the polymer of all aromatic polyamide as the base material configuration, textiles, the sheet of Mr. Kami who has the permeability which the synthetic pulp which is the polymer of all aromatic polyamide distributes in the clearance between the aramid fiber, or the polymer of all aromatic polyamide opened etc. can be mentioned. If the need property as the above mentioned base material is satisfied, it is possible to use the thing of every configuration for this invention among these, but when air permeability is taken into consideration, a nonwoven fabric-like sheet is used most suitably. As the amount of superintendent officers, the range of 12 - 30 g/m² is used suitably. Although it becomes easy to obtain the high base material of air permeability when the amount of superintendent officers is less than [12g //m] two, it becomes difficult to thrust and to obtain a thing 200g or more as reinforcement, and it becomes impossible to obtain the solid-state mold electrolyte membrane which was excellent in the mechanical characteristic as a result. On the other hand, although it will become easy to thrust and to satisfy reinforcement if the amount of superintendent officers increases more than 30 g/m², it becomes difficult to obtain the base material of 50 micrometers or less of average thickness. Moreover, if a consistency is formed into a raising thin film by force, it becomes difficult and is not desirable for air permeability to fall and to obtain the high bipolar membrane of proton

conductivity as a result.

[0020] As the molecular structure of all aromatic polyamide polymers, it is available to this invention regardless of a metasystem and the Para system. With a metasystem, all the aromatic polyamide that makes m-phenylene isophthalamide a main configuration unit is mentioned as a typical thing, and it is mentioned here as what has all the aromatic polyamide typical [the Para system] that makes p-phenylene terephthalamide a main configuration unit.

[0021] Moreover, the porosity base material of this invention may cover the front face with a metallic oxide etc. if needed, and may raise the oxidation resistance of a base material. The coat by the metallic oxide can be performed by immersing said porous base material thin film in the gel product solutions (alcohol etc.) of the shape of a solution which made hydrolysis nature organic metal compounds, such as a metal alkoxide, react with water, and made them specifically gel selectively, being immersed subsequently to water, and drying at the temperature around [after promoting a reaction] 200 degrees C.

[Translation done.]

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EXAMPLE

[Example] Hereafter, the content of this invention is explained to a detail using an example.

[0023] [Example 1]

The amorphous-ized m-aramid continuous glass fiber of size 3de was added as a binder to m-aramid staple fiber which <aramid base material> size 1.25de crystallized, the film was produced by amount of superintendent officers 19 g/m² by the dry type milling-paper method, the calendering roll was covered, and the nonwoven fabric-like sheet was obtained. The property of the obtained base material was as follows. 36 micrometers of average thickness, consistency 0.53 g/cm³, 62% of voidage, and air permeability 0.04sec/100 cc-in² — thrusting — the reinforcement of 330g.

[0024] Using perphloro sulfonic-acid (Nafion) resin as polymer resin for the electrolytes of <compound-ized of polymer electrolyte> proton conductivity, 5% solution (Nafion; Aldrich make) of this was dried at 80 degrees C after impregnation and coating to the aforementioned aramid base material for 2 hours, and the Nafion bipolar membrane was produced. The property of the obtained bipolar membrane was as follows. 40 micrometers of thickness, and the 60 % of the weight of the amounts of Nafion impregnation, it thrusts and they are the reinforcement of 450g, and the TMA heatproof temperature of 400 degrees C or more.

[0025] Using the electrode made from U.S. E-TEKINC which made the platinum of 0.38 mg/cm² support as a <fuel cell cel production> gas diffusion electrode, this was pierced to 30mmphi and it considered as the gas diffusion electrode. After being immersed for 2 hours into the ion exchange water which boiled the aforementioned compound electrolyte membrane and making the film into a moisture state, surface superfluous water was wiped off, and it put with two gas diffusion electrodes, and pressurized for 3 minutes by 100 Kgf/cm² at 100 degrees C, and the electrode zygote was obtained. About the obtained electrode complex, humidification hydrogen and oxygen were supplied and fuel cell output characteristics were evaluated under 80-degree-C heating. Although ten single cels were produced, defects, such as a short circuit and a gas leak, do not have one, and the engine performance of 0.65V was obtained by 0.7 A/cm².

[0026] The electrolyte membrane of Nafion independent 40-micrometer thickness was produced without using an aramid base material in the [example 1 of comparison] example 1. The fuel cell single cel was produced like the example 1 using the obtained film. The defect (a short circuit, gas leak) was accepted in three of ten produced single cels, and production of the stable thin film cel was difficult.

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最終頁に続く

(54) 【発明の名称】 固体型ポリマー電解質膜

(57) 【要約】

【課題】 機械強度と耐熱性に優れた燃料電池に適した固体型ポリマー電解質膜。

【解決手段】 膜の突刺し強度が300g以上であり、かつ膜の力学的な耐熱温度が300℃以上である、多孔質薄膜とプロトン伝導性のポリマー電解質との複合体からなる固体型ポリマー電解質膜。

【特許請求の範囲】

【請求項1】 膜の突刺し強度が300g以上であり、かつ膜の力学的な耐熱温度が300℃以上であるプロトン伝導性の固体型ポリマー電解質膜。

【請求項2】 多孔質薄膜とプロトン伝導性のポリマー電解質との複合体である、請求項1の固体型ポリマー電解質膜。

【請求項3】 該固体型ポリマー電解質膜におけるプロトン伝導性ポリマー電解質の含有量が30～85重量%であることを特徴とする請求項1～2記載の固体型ポリマー電解質膜。

【請求項4】 該多孔質薄膜が、平均膜厚が50μm以下で、突刺し強度が200g以上で、かつ透気度が10sec/100cc・in²以下の高強度・高透気度の多孔質薄膜支持体であることを特徴とする請求項2～3記載の固体型ポリマー電解質膜。

【請求項5】 該高強度・高透気度の多孔質薄膜支持体が、全芳香族ポリアミド重合体であるアラミド繊維からなる不織布、織物、あるいはアラミド繊維の隙間に全芳香族ポリアミドの重合体である合成パルプが分散する構造の通気性のある紙様のシート、あるいはアラミド樹脂からなる細孔が多数開いたフィルムであることを特徴とする請求項4記載の固体型ポリマー電解質膜。

【請求項6】 該高強度・高透気度の多孔質薄膜支持体が、全芳香族ポリアミド重合体からなる目付け量12～30g/m²の不織布状のシートであることを特徴とする請求項5記載の固体型ポリマー電解質膜。

【請求項7】 該複合体が、多孔質薄膜とポリマー電解質との含浸一体化複合体である、請求項2～6の固体ポリマー電解質膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、機械強度と耐熱性に優れた燃料電池に適した固体型ポリマー電解質膜に関するものである。

【0002】

【従来の技術】近年、環境問題のクローズアップとともに新エネルギー技術が脚光を浴びてきている。燃料電池技術は、これら新エネルギー技術の柱の一つとして位置づけられている。中でも電解質としてプロトン伝導性の高分子電解質膜を用いた固体高分子型燃料電池(PEFC)は、小型軽量化が可能等の特徴から、電気自動車をはじめとする搭載用の電源として注目されている。

【0003】固体高分子型燃料電池用の高分子電解質膜としては、例えば超強酸基含有のパフフロポリマーであるナフィオン[®](Nafion 115、117など、デュポン社登録商標)が知られている。これは、イオン交換容量が0.9lミリ当量/g樹脂と比較的高いだけでなく、機械的強度も比較的優れている材料として広く利用されている。これを用いた燃料電池において取り出せる電流密度は電解

質膜の抵抗に依存しており、膜を薄膜化し水の膨潤度を高めるほど、膜抵抗が低下し大きな電流が取り出せることが知られている。しかしながら、この電解質膜を用いた場合でも、前記の観点から膜厚を薄くすると、例えばホットプレス法により電解質膜と電極とを接合させる際に、膜が破損しガスのリークを生じたり、電極間の短絡が生じる問題があった。また、この問題を回避する目的で、ホットプレスを用いずに機械的に電解質膜を挟み込みセルを組み立てる方法も提案されている。しかし、この手法を採用した場合でも、電極との接合を一定に保つためには、かなりの圧力を掛けることが必要で、ホットプレス法と同様の問題点を有していた。また、どうにかセルを組み立てた場合でも、電解質膜の水膨潤状態での機械強度が十分でないために、長期の使用において短絡かガスリークを併発するなどの問題があった。

【0004】上記のように、ナフィオン[®]に代表される電解質膜の機械特性(セル作製時および水膨潤状態時)を改善する方法として、特開平8-162132号公報には、延伸テトラフロエチレン多孔膜空隙部に該高分子電解質を含浸一体化し、電解質膜の機械特性を補強した複合型電解質膜が記載されている。しかし、この技術の場合、支持体として採用している多孔膜が高価なだけでなく、その表面張力が小さいために、実際の電解質ドープを含浸する際のドープの濡れ性の問題から、ドープが含浸し難い問題点を有していた。

【0005】

【発明が解決しようとする課題】前述したように固体高分子型燃料電池の実用化の観点から、機械特性の優れた薄膜化可能なプロトン伝導性のポリマー電解質膜の開発が検討されているが、未だに実用的に優れたポリマー電解質膜は見出されていない状況にある。

【0006】このような状況を鑑み鋭意検討した結果、実用的な高いプロトン伝導性と、セパレータとしての強い短絡防止強度と、短絡防止に関しての高い耐熱性とを兼ね備えた実用面で優れた固体型ポリマー電解質膜を開発する方法を見出し、本発明を完成するに至った。本発明の目的は、プロトン伝導性と、強度と、耐熱性の三者を兼ね備えた、燃料電池用の固体型ポリマー電解質膜を提供することにある。

【0007】

【課題を解決するための手段】本発明は、突刺し強度が300g以上であり、かつ膜の力学的耐熱温度が300℃以上であるプロトン伝導性の固体型ポリマー電解質であり、それは多孔質薄膜とプロトン伝導性ポリマー電解質との複合体からなるものである。該固体型ポリマー電解質膜におけるポリマー電解質の含有量は30～85重量%であることが好ましい。また、該多孔質薄膜が、平均膜厚が50μm以下で、突刺し強度が200g以上で、かつ透気度が10sec/100cc・in²以下の高強度・高透気度の多孔質薄膜支持体であること、その高強度・高透気度の多孔質薄膜支持

体は、全芳香族ポリアミド重合体であるアラミド繊維からなる不織布、織物、あるいはアラミド繊維の隙間に全芳香族ポリアミドの重合体である合成パルプが分散する構造の通気性のある紙様のシート、あるいはアラミド樹脂からなる細孔が多数開いたフィルムであること、又は、該高強度・高透気度の多孔質薄膜支持体は、全芳香族ポリアミド重合体からなる目付け量12~30g/m²の不織布状のシートであることが好ましく、さらには該複合体は、多孔質薄膜とポリマー電解質との含浸一体複合体であることが好ましい。

【0008】

【発明の実施の形態】以下、本発明の固体型ポリマー電解質に関して更に説明する。本発明の固体型ポリマー電解質膜は、燃料電池に適用するに十分な300g以上の突刺し強度を示し、かつ300℃以上の力学的な耐熱温度を有する実用的なプロトン伝導性と優れた熱機械特性とを兼ね備えたポリマー電解質膜である。

【0009】本発明の固体型ポリマー電解質膜の場合、突刺し強度が300g以上と高いことも特徴である。突刺し強度は、現状の溶液型リチウムイオン二次電池のセパレータの短絡防止強度を表す指標としてセパレータの評価に利用されている物性であり、本発明においては、下記の条件にて測定した値を突刺し強度とした。

【0010】固体型ポリマー電解質膜を11.3mmφの固定枠にセットし、先端部半径0.5mmの針を支持体の中央に垂直に突き立て、50mm/分の一定速度で針を押し込み、支持体に穴が開いた時の針にかかっている力を突刺し強度とした。

【0011】この値が300g未満の場合、このポリマー電解質膜の突刺し強度が十分でなくなり、電池を組み上げる際のホットプレス工程での電極同士の短絡発生確率や膜のガスリーク確率が上がり好ましくなくなる。

【0012】また、本発明のポリマー電解質膜は、300℃以上の力学的な耐熱性を有している点が特徴である。ここで、力学的な耐熱温度は、以下の条件で測定した。

【0013】膜厚約45μm、幅5mm、長さ25mmの短冊状のポリマー電解質膜に1gの荷重をかけ、即ち0.0044g/μm・mmの荷重で10℃/分の速度で温度を昇温させ熱機械的特性分析(TMA)を実施し、膜が破断するか、あるいは膜が10%伸びる温度を力学的な耐熱温度とした。

【0014】この温度が300℃未満では、異常反応等により、電池の内部温度が急激に上がった際の電池の安定性を保証できなくなり好ましくない。本発明の、固体型ポリマー電解質膜は、強度、耐熱性に特徴のある多孔質支持体薄膜と実用的に十分なプロトン伝導性を有するポリマー電解質を複合化することにより作製される。その際のポリマー電解質の含有量は、30~85重量%の範囲が好ましい。ポリマー電解質含有量が30重量%未満では、多孔質支持体と複合化した際に十分なプロトン伝導性が得られず好ましくない。また、その含有量が85重量%よ

り多くなると、複合膜の強度が低下したり、あるいは、ポリマー電解質膜の膜厚が増加し好ましくなくなる。

【0015】次に、本発明の多孔質支持体に含浸複合化させるプロトン伝導性のポリマー電解質について説明する。本発明に利用するポリマー電解質としては、特に限定されるものではなく、従来機械特性的に問題があるとされていた高いイオン交換基当量を有するプロトン伝導性ポリマー電解質も多孔質支持体の併用により可能である。具体的なポリマー電解質としては、ナフィオン[®]に代表されるようなパーフロロ骨格を有するスルホン酸ポリマーや、スルホン化ポリスルホン、スルホン化ポリエーテルスルホン、スルホン化ポリエーテルエーテルケトンなどが挙げられる。但し、製膜工程の容易さから、流動(溶液)状態のポリマーから多孔質薄膜支持体に直接含浸塗工できるタイプのポリマーがより好適に用いられる。

【0016】次に、本発明に用いる多孔質支持体薄膜について説明する。本発明の多孔質支持体薄膜としては、平均膜厚が50μm以下で、突刺し強度が200g以上で、かつ透気度が10sec/100cc・in²以下の高強度・高透気度薄膜が好適に用いられる。平均膜厚が50μm以上になれば、高強度の支持体を得ることは容易となるが、得られるポリマー電解質複合膜の膜厚が厚くなるため、電解質膜の水に対する膨潤度が低下し、膜抵抗が上がり好ましくなくなる。

【0017】本発明の支持体の突刺し強度としては、200g以上のものが好適に用いられる。この値が、200gより低い支持体を用いた場合は、ポリマー電解質を含浸させ複合化した後でも300g以上の突刺し強度を実現することが困難となりこのましくない。

【0018】本発明の支持体の透気度は、ガーレー法(100ccの空気が1in²の面積を2.3cmHgの圧力で透過するに要する時間)により測定した値を示している。本発明の多孔質支持体薄膜としては、この値が、10sec/100cc・in²以下の高い透気度を示す支持体が好適に用いられる。この値が、10sec/100cc・in²よりも大きい透気度の低い支持体を用いた場合、工業的に最も有利と考えられるポリマー溶液からの塗工法によるポリマー電解質の含浸複合化が困難となるとともに、複合ポリマー電解質のプロトン伝導性も十分に高めることが困難になり好ましくない。

【0019】本発明の高強度・高透気度の多孔質薄膜支持体用の材料としては、強度と耐熱性の観点から全芳香族のポリアミドが好ましく用いられる。その支持体形状としては、全芳香族ポリアミドの重合体であるアラミド繊維からなる不織布、織物、あるいは、そのアラミド繊維の隙間に全芳香族ポリアミドの重合体である合成パルプが分散する通気性のある紙様のシート、あるいは、全芳香族ポリアミドの重合体であるアラミド樹脂からなる孔が多数開いた通気性のあるフィルム等を挙げるこ

出来る。前記した支持体としての必要特性を満足しておれば、これらの内どの形状のものも本発明に利用することが可能であるが、透気度を考慮した場合、不織布状のシートが最も好適に用いられる。その目付け量としては、 $12\sim 30\text{g}/\text{m}^2$ の範囲が好適に用いられる。目付け量が $12\text{g}/\text{m}^2$ 未満の場合、透気度の高い支持体を得るのは容易となるが、突刺し強度として 200g 以上のものを得ることが困難となり、結果的に機械特性の優れた固体型電解質膜を得ることが出来なくなる。一方、目付け量が $30\text{g}/\text{m}^2$ よりも多くなると、突刺し強度を満足することは容易となるが、平均膜厚 $50\mu\text{m}$ 以下の支持体を得ることが困難となる。また、無理に密度を上げ薄膜化すると、透気度が低下し結果的にプロトン伝導性の高い複合膜を得ることが困難になり好ましくない。

【0020】全芳香族ポリアミド重合体の分子構造としては、メタ系、パラ系を問わず本発明に利用可能である。ここでメタ系とは、 m -フェニレンイソフタルアミドを主たる構成単位とする全芳香族ポリアミドが代表的なものとして挙げられ、パラ系とは、 p -フェニレンテレフタルアミドを主たる構成単位とする全芳香族ポリアミドが代表的なものとして挙げられる。

【0021】また、本発明の多孔質支持体は必要に応じその表面を金属酸化物等で被覆し、支持体の耐酸化性を向上させてもよい。具体的には、金属アルコキシド等の加水分解性金属有機化合物を水と反応させ部分的にゲル化させた溶液状のゲル生成物溶液(アルコールなど)に前記多孔性支持体薄膜を浸漬し、次いで水に浸漬し反応を促進後、 200°C 前後の温度で乾燥を行なうことにより、金属酸化物による被覆を行なうことができる。

【0022】

【実施例】以下、本発明の内容を実施例を用い詳細に説明する。

【0023】〔実施例1〕

<アラミド支持体>太さ 1.25de の結晶化させた m -アラミド短繊維に太さ 3de の非結晶化 m -アラミド長繊維を

バインダーとして添加し、乾式抄造法により目付け量 $19\text{g}/\text{m}^2$ で製膜しカレンダーロールをかけ不織布状のシートを得た。得られた支持体の特性は以下の通りであった。平均膜厚 $36\mu\text{m}$ 、密度 $0.53\text{g}/\text{cm}^3$ 、空隙率 62% 、透気度 $0.04\text{sec}/100\text{cc}\cdot\text{in}^2$ 、突刺し強度 330g 。

【0024】<ポリマー電解質の複合化>プロトン伝導性の電解質用のポリマー樹脂としてパーフロスルホン酸(ナフィオン)樹脂を用い、これの 5% 溶液(ナフィオン;アルドリッチ社製)を前記のアラミド支持体中含浸・塗工後 80°C にて2時間乾燥し、ナフィオン複合膜を作製した。得られた複合膜の特性は以下の通りであった。膜厚 $40\mu\text{m}$ 、ナフィオン含浸量 $60\text{重量}\%$ 、突刺し強度 450g 、TMA耐熱温度 400°C 以上。

【0025】<燃料電池セル作製>ガス拡散電極として $0.38\text{mg}/\text{cm}^2$ の白金を担持させた米国E-TEKINC製の電極を用い、これを $30\text{mm}\phi$ に打ち抜きガス拡散電極とした。前記の複合電解質膜を沸騰したイオン交換水中に2時間浸漬し、膜を含水状態とした後、表面の過剰の水を拭き取り、ガス拡散電極2枚で挟み込み、 100°C にて $100\text{Kg}/\text{cm}^2$ で3分間加圧し電極接合体を得た。得られた電極複合体について、加湿水素及び酸素を供給し 80°C 加熱下で燃料電池出力特性を評価した。10ケの単セルを作製したが、短絡やガスリークなどの欠陥は一つもなく、 $0.7\text{A}/\text{cm}^2$ で 0.65V の性能が得られた。

【0026】〔比較例1〕実施例1においてアラミド支持体を用いずに、ナフィオン単独の $40\mu\text{m}$ 膜厚の電解質膜を作製した。得られた膜を用い、実施例1と同様にして燃料電池単セルを作製した。作製した10ケの単セルの内3ケに欠陥(短絡、ガスリーク)が認められ、安定した薄膜セルの作製が困難であった。

【0027】

【発明の効果】本発明によれば、優れたプロトン伝導性と、優れた熱機械特性とを有する固体高分子型燃料電池用途に有用な固体型ポリマー電解質膜を提供することが可能となる。

フロントページの続き

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